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(54) Low-pressure Mercury Vapour Discharge Lamp

(57) Low-pressure mercury vapour discharge lamp suitable for use in photo-therapy and having a glass discharge tube which is opaque to shorter wavelength ultraviolet radiation and bearing a luminescent layer on its inside surface. A problem in such lamps is to produce a useful quantity of radiation which is effective for photo-therapy in combination with as low a quantity of erythema-producing radiation as possible. The luminescent layer comprises a luminescent material having the characteristic line emission of gadolinium at 312 nm, and the glass has an absorption edge located between 260 and 280 nm and a transmission at 312 nm of at least 80%. Suitable phosphors are specified e.g. LaGdBi borate, SrPbLaGd silicate and GdPbMg aluminate; as are suitable glasses.

GB 2 054 951 A

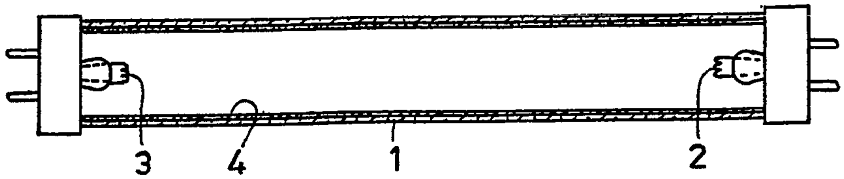

FIG. 1

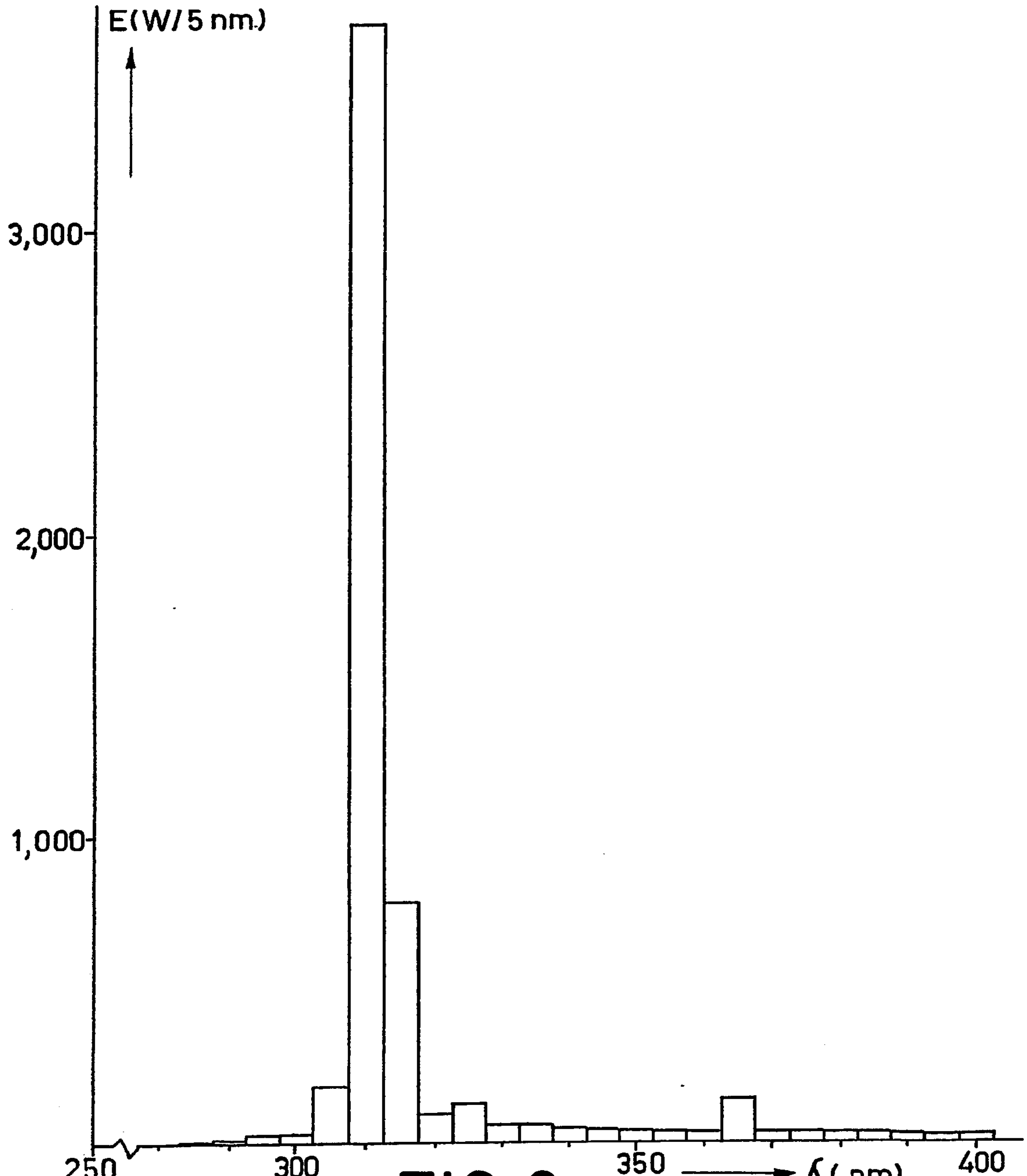

FIG. 2

SPECIFICATION
Low-Pressure Mercury Vapour Discharge Lamp

The invention relates to a low-pressure mercury vapour discharge lamp for radiation purposes having a discharge tube made of glass with a selective transmission, the tube being coated on the inside with a luminescent layer.

It is known that radiation in the wavelength range from 305—320 nm may have a favourable therapeutic effect, for example in the treatment of psoriasis and other skin diseases (see an article by H. Tronnier *et al* in Afinidaed, May 1977, pages 285—290. A lamp of the type defined in the opening paragraph, intended to radiate selectively in the above-mentioned wavelength range is disclosed in German Patent Application 2,707,894 which has been laid open to public inspection. The known lamp is provided with a luminescent layer of a luminescent, cerium-activated strontium aluminate. Cerium-activated aluminates, which are described in Netherlands Patent Application 7214862 and 7401935 (to which United Kingdom Patent Specifications 1,452,083 and 1,476,902 respectively correspond) have a comparatively wide emission band (half-value width approximately 45 nm) with a maximum at approximately 310 nm, so that approximately half of the radiation emitted by these materials is located in the UVB-portion of the erythema range (290—315 nm). At the maximum erythema sensitivity (approximately 297 nm) the intensity of the radiation emitted from these materials is still approximately 75% of the peak value at 310 nm. As generally only a small quantity of erythema radiation is permissible for photo-therapy, the discharge tube bearing the luminescent layer in the known lamp is made of a glass having a selective transmission. Specifically, this glass must have an absorption edge at approximately 295 nm, that is to say there is substantially no transmission below 295 nm.

The known lamp has the serious drawback that the radiation efficiency is very low, as more than 60% of the radiation emitted by the luminescent material is absorbed by the wall of the discharge tube. It furthermore appears that the selectivity of the radiation emitted by the lamp is not very high. It appeared that for each watt of total radiation emitted in the ultraviolet portion of the spectrum (250—400 nm), the lamp produces only 0.14 watt of useful radiation in the range from 307.5 to 317.5 nm. Consequently, long irradiation times are necessary for photo-therapy treatments with all the drawbacks that this entails. A further drawback of the known lamp, also owing to the poor selectivity, is that the quantity of erythema radiation emitted by the lamp is considerably above the minimum quantity which is theoretically possible. Since the erythema sensitivity curve (as defined by the Commission Internationale de l'Eclairage) in the range from 307.5 to 317.5 nm has values ranging from 20% to almost 0%, radiation in this wavelength range also shows erythema activity. Radiation having, for example, an equi-energy spectrum in this range has approximately 0.08 erythema watt per watt, which is then the lowest quantity which can be obtained. However, the known lamp appears to radiate approximately 0.17 erythema watt per watt of useful radiation. For a given permissible erythema load, this means a limitation of the dose of useful radiation per treatment and, consequently, an increase in the number of treatments required.

It is an object of the invention to provide a lamp for radiation purposes having a high radiation efficiency in the range from 307.5 to 317.5 nm and improved selectivity with respect to erythema-producing radiation.

The invention provides a low-pressure mercury vapour discharge lamp for radiation purposes having a glass discharge tube bearing a luminescent layer on its inside surface, the luminescent layer comprising a luminescent material having the characteristic line emission of gadolinium at 312 nm, and wherein the glass has an absorption edge located between 260 and 280 nm, and a transmission at 312 nm of at least 80%.

The invention is based on the recognition of the fact that a high radiation efficiency and a high selectivity can only be obtained when very severe requirements are imposed on the luminescent material to be used. In addition to a high efficiency on excitation by 254 nm radiation, the material must have an emission which is substantially wholly concentrated in the range from 305—320 nm, substantially all the radiation emitted by the material then being useful radiation, so that it is not then necessary to use a filter having an absorption edge at approximately 295 nm (which is close to the lower limit of the range of desired radiation) to limit the erythema radiation. It appeared that materials having the characteristic line emission of gadolinium at 312 nm satisfy these conditions. The Gd-ion has a characteristic emission spectrum, that is to say the spectrum is only dependent on the host lattice in which the luminescent ion is incorporated to a small extent. The Gd-emission consists of a very narrow band (actually some closely adjacent emission lines) with a maximum at approximately 312 nm. The half-width value of this emission band is only 2 to 4 nm. Furthermore the Gd-luminescence appears to occur very efficiently in different host lattices.

Although an absorption filter for erythema radiation is superfluous in a lamp according to the invention, the discharge tube must yet have a selective transmission in order to prevent the mercury-resonance radiation produced in the lamp at 185 nm and predominantly at 254 nm, from being emitted from the lamp. Specifically, the glass of this tube must have an absorption edge located between 260 and 280 nm. This means that the transmission curve of the glass at a wavelength in the range from 260 to 280 nm

reaches a value of 10%, and still lower values below that wavelength. This guarantees that substantially no radiation is transmitted below 260 nm. Furthermore, the glass tube must have at 312 nm a transmission of at least 80%. The requirement that the glass has a transmission of at least 80% at 312 nm ensures that the transmission curve is sufficiently steep and that the majority of the Gd-radiation is transmitted.

With a lamp according to the invention it is possible to obtain a high radiation efficiency as not more than 20%, and with an optimum choice of the glass for the discharge tube a much lower quantity, of the radiation emitted by the luminescent material is absorbed by the tube wall. This is a considerable improvement compared with the known lamp, in which more than 60% of the radiation emitted by the luminescent material is absorbed. A further considerable advantage of a lamp according to the invention is its excellent selectivity. Instead of the emitted radiation of the known lamp of only 0.14 watt of useful radiation (307.5—317.5 nm) per watt in the UV (250—400 nm), this fraction of useful radiation is a factor of 5 to 6 higher, namely 0.70 to 0.80 watt per watt in a lamp according to the invention. The very good selectivity of the lamp is also apparent from the low fraction of erythema radiation which depending on the glass used for the discharge tube, appears to be only 0.10 to 0.13 erythema watt per watt of useful radiation, which values approach the theoretically possible minimum quantities very closely.

In one aspect of the invention, the luminescent layer contains a borate, activated by Gd and Bi and having a composition defined by the formula

$$La_{1-x-y}Gd_xBi_yB_3O_6,$$

wherein $0.15 \leq x$, $0.001 \leq y \leq 0.05$ and $x+y \leq 1$. These borates which are further described in Netherlands Patent Application 7607724 (which corresponds to United Kingdom Patent Specification 1,536,637), emit very efficiently the characteristic Gd-radiation. On excitation by the mercury resonance radiation having a wavelength of approximately 254 nm, quantum efficiencies of 70 to 75% can be obtained with these materials.

In another aspect of the invention, the luminescent layer contains a ternary aluminate activated by Gd and Pb and having a hexagonal magneto-plumbite structure, the aluminate having the composition ABC wherein A represents 25—99 mole % $\frac{1}{2}$ Gd_2O_3, 1—35 mole % PbO, the balance if any consisting of $\frac{1}{2}$ La_2O_3, wherein B represents Al_2O_3, not more than 20 mole % of the Al_2O_3 having been replaced by Sc_2O_3, and wherein C represents MgO and/or ZnO, up to 10 mole % of the Al_2O_3 possibly having been replaced by a chemically equivalent quantity of a combination of equimolar quantities of SiO_2 and (MgO and/or ZnO), up to 70 mole % of A possibly having been replaced by SrO and/or CaO and, simultaneously an equivalent quantity of C by $\frac{1}{2}$ Al_2O_3, and wherein the contents A, B and C satisfy the conditions $[A] \geq 0.02$, $0.55 \leq [B] \leq 0.95$ and $[C] \geq \frac{1}{2}[A]$. and $[A]+[B]+[C]=1$. These luminescent aluminates are further described in Netherlands Patent Application 7811436 (and which corresponds to our co-pending application 7939798) and appear to have high quantum efficiencies. The materials defined by the formulae

$$Gd_{0.90}Pb_{0.15}MgAl_{11}O_{19}$$

and

$$Gd_{0.88}Pb_{0.18}ZnAl_{11}O_{19},$$

for example, have quantum efficiencies of (254 nm-excitation) of 50 to 55%.

In a further aspect of the invention, the luminescent layer contains a silicate of Sr and/or Ca and of Y and/or La and activated by Gd and Pb having a composition defined by the formula

$$(Sr, Ca)_{3-p}Pb_p(Y,La)_{2-q}Gd_qSi_6O_{18},$$

wherein $0.01 \leq p \leq 0.50$ and $0.05 \leq q \leq 2.0$. At 254 nm-excitation, these silicates have a quantum efficiency for the Gd luminescence of approximately 60%.

It is conceivable that quartz glass or a glass consisting predominantly of SiO_2 may be used as the glass for the discharge tube of a lamp according to the invention, the absorption edge having been shifted to the range from 260 280 nm by the addition of small quantities of other elements.

Preference is, however, given to a low-pressure mercury vapour discharge lamp according to the invention the glass of its discharge tube containing

68—78.9 mole % SiO_2,
2.5—3.0 mole % B_2O_3,
16—20 mole % of at least one alkali metal oxide,
2.6—3.3 mole % of at least one alkaline earth metal oxide,
0—2.0 mole % Al_2O_3,

and furthermore at least one of the oxides TiO_2, CeO_2, CuO, Fe_2O_3 and V_2O_5 in a small quantity, such that the absorption edge of the glass is located between 260 and 280 nm. The glasses having the above-defined basic compositions (that is to say the compositions defined above but excluding TiO_2, CeO_2, CuO, Fe_2O_3 and V_2O_5) which must be prepared from chemically pure materials, have a very short-wave absorption edge, for example at 210 nm, so that they pass ultra-violet radiation up to relatively short wavelengths. By the addition of a small quantity of one or more of the oxides TiO_2, CeO_2, CuO, Fe_2O_3 and V_2O_5 to such a basic composition, the absorption edge of the glass can be adjusted between comparatively wide limits. According as the quantity used of the above oxides is greater the absorption edge

will be found at longer wavelengths. The glasses to be used for the lamps according to the invention generally contain a total of from 100 to 2500 ppm by weight of the said oxides. These glasses have the further advantage that they have a transmission curve which is sufficiently steep so that the majority of the desired useful radiation is transmitted. Furthermore, these glasses have suitable properties for making discharge tubes of low-pressure mercury vapour discharge lamps.

A particularly advantageous glass composition for the discharge tube of a low-pressure mercury vapour discharge lamp, according to the invention consists of

75.5 ± 2 mole % SiO_2
2.8 ± 0.1 mole % B_2O_3
10.2 ± 0.3 mole % Na_2O
7.7 ± 0.3 mole % K_2O
3.0 ± 0.1 mole % BaO
1.0 ± 0.03 mole % Al_2O_3, and, in addition, of 500—2000 ppm by weight of TiO_2.

Some embodiments of lamps according to the invention will now be described with reference to the following Examples and to a drawing in which:—

Figure 1 is a schematic longitudinal sectional view of a lamp according to the invention and

Figure 2 shows by means of a graph the spectral energy distribution of the emitted radiation of such a lamp.

The lamp shown in Figure 1 has a glass discharge tube 1 which is approximately 1200 mm long and has an outside diameter of approximately 38 mm. The wall thickness of the tube 1 is approximately 0.75 mm. The glass of the discharge tube 1 has the following composition:

75.46 mole % (68.4% by weight) SiO_2,
2.76 mole % (2.9% by weight) B_2O_3,
10.17 mole % (9.5% by weight) Na_2O,
7.68 mole % (10.9% by weight) K_2O,
2.94 mole % (6.8 by weight) BaO,
0.97 mole % (1.5% by weight) Al_2O_3,
900 wt. ppm TiO_2.

At approximately 265 nm this glass has a transmission of 10%. At 312 nm the transmission of the glass is 85 to 90%. Electrodes 2 and 3 are provided, one at each end of the lamp, the discharge taking place during operation between these electrodes. The lamp contains a mixture of rare gases as the starting gas, and a small quantity of mercury. The inside surface of the tube 1 is coated with a luminescent layer 4 comprising a luminescent material which emits the characteristic 312 nm radiation of Gd. The layer 4 can be applied in a customary manner to the tube 1, for example by means of a suspension containing the luminescent material. During operation the lamp consumes a power of 40 W.

Example 1

A number of lamps of the type described above with reference to Figure 1 were coated with a layer of luminescent borate having a composition defined by the formula

$$La_{0.487}Gd_{0.5}Bi_{0.013}B_3O_6.$$

After having been in operation for 100 hours it appeared that these lamps emitted over the whole ultraviolet portion of the spectrum (from 250—400 nm) a quantity of radiation totaling 5.603 W. The quantity of useful radiation in the range from 307.5 to 317.5 nm appeared to be 4.460 W, that is to say approximately 80% of the total emitted radiation is useful radiation. Figure 2 is a graphical representation of the spectral energy distribution of the radiation emitted by this lamp. The wavelength λ in nm is plotted on the horizontal axis, the emitted radiant energy E being plotted on the vertical axis in W per wavelength interval of 5 nm.

Example 2

Lamps having a construction as described with reference to Figure 1 but having a 1500 mm long tube and intended to consume a power of 80 W, were coated with a luminescent layer of the same luminescent material as used in Example 1. After having been in operation for 100 hours a total (250—400 nm) emitted quantity of radiation of 11.2 W was measured on these lamps. It appeared that 8.0 W (71.5%) was emitted in the range from 307.5—317.5 nm. The quantity of erythema radiation emitted by the lamp appeared to be 0.92 erythema watt, that is to say only approximately 11.5% of the total quantity of useful radiation. For comparison, the known lamps having a construction similar to the lamps described above but having discharge tubes made of glass having an absorption edge at approximately 300 nm and using a luminescent cerium-activated strontium aluminate as the luminescent material, emit in total (250—400 nm) a radiation of 5.9 W (that is only approximately 33% of the radiation generated in the luminescent material). However, only approximately 0.83 W (that is to say approximately 14%) of this quantity of radiation is located in the range from 307.5—317.5 nm. In addition, it appeared that the quantity of erythema radiation emitted by the known lamp was 16.7% of the quantity of useful radiation (namely approximately 0.14 erythema watt). When the lamps according to the invention are used for phototherapy it is therefore possible to use a treatment time which is shorter by a factor of 10 for the same dose of useful radiation, while the erythema dose is reduced by approximately 35%, compared with the last-mentioned known lamp.

Example 3

A number of lamps of the type shown in Figure 1 were coated with a luminescent layer of a luminescent silicate having a composition defined by the formula

$$Sr_{2.9}Pb_{0.1}LaGdSi_6O_{18}.$$

After having been in operation for 100 hours a quantity of radiation of 4.96 W, emitted over the whole ultra violet portion of the (250—400 nm) spectrum was measured on these lamps. It appeared that 3.95 W thereof was emitted in the range from 307.5 to 317.5 nm. It appeared that for these lamps the spectral energy distribution of the emitted radiation was substantially equal to those of the lamps described in Example 1.

Claims

1. A low-pressure mercury vapour discharge lamp for radiation purposes having a glass discharge tube bearing a luminescent layer on its inside surface, the luminescent layer comprising a luminescent material having the characteristic line emission of gadolinium at 312 nm, and wherein the glass has an absorption edge located between 260 and 280 nm. and a transmission at 312 nm of at least 80%.

2. A low-pressure mercury vapour discharge lamp as claimed in Claim 1, characterised in that the luminescent layer contains a borate activated by Gd and Bi, this borate having a composition defined by the formula $La_{1-x-y}Gd_xBi_yB_3O_6$, wherein $0.15 \leq x$, $0.001 \leq y \leq 0.05$ and $(x+y) \leq 1$.

3. A low-pressure mercury vapour discharge lamp as claimed in Claim 1, characterised in that the luminescent layer contains a ternary aluminate activated by Gd and Pb and having the hexagonal magneto-plumbite structure, the aluminate having the composition ABC, wherein A represents from 25—99 mole % $\frac{1}{2}$ Gd_2O_3, 1—35 mole % PbO, the balance if any consisting of $\frac{1}{2}$ La_2O_3, wherein B represents Al_2O_3, not more than 20 mole % of the Al_2O_3 having been replaced by Sc_2O_3 and wherein C represents MgO and/or ZnO, up to 10 mole % of the Al_2O_3 possibly having been replaced by an equivalent quantity of SiO_2 together with MgO and/or ZnO, up to 70 mole % of A possibly having been replaced by SrO and/or CaO and, simultaneously, an equimolar quantity of C by $\frac{1}{2}$ Al_2O_3, the contents A, B and C satisfying the conditions $[A] \geq 0.02$, $0.55 \leq [B] \leq 0.95$ and $[C] \geq \frac{1}{2}[A]$.

4. A low-pressure mercury vapour discharge lamp as claimed in Claim 1, characterised in that the luminescent layer contains a Gd and Pb-activated silicate of Sr and/or Ca and of Y and/or La defined by the formula

$$(Sr,Ca)_{3-p}Pb_p(Y,La)_{2-q}Gd_qSi_6O_{18},$$

wherein $0.01 \leq p \leq 0.50$ and $0.05 \leq q \leq 2.0$.

5. A low-pressure mercury vapour discharge lamp as claimed in any of Claims 1 to 4, characterised in that the glass of the discharge tube contains

68—78.9 mole % SiO_2,
2.5—3.0 mole % B_2O_3,
16—20 mole % of at least one alkali metal oxide,
2.6—3.3 mole % of at least one alkaline earth metal oxide,
0—2.0 mole % Al_2O_3, and further at least one of the oxides TiO_2, CeO_2, CuO, Fe_2O_3 and V_2O_5 in a small quantity such that the absorption edge of the glass is between 260 and 280 nm.

6. A low-pressure mercury vapour discharge lamp as claimed in Claim 5, characterised in that the glass consists of

75.5±2 mole % SiO_2
2.8±0.1 mole % B_2O_3
10.2±0.3 mole % Na_2O
7.7±0.3 mole % K_2O
3.0±0.1 mole % BaO
1.0±0.03 mole % Al_2O_3 and, in addition, 500—2000 wt. ppm TiO_2.

7. A low-pressure mercury vapour discharge lamp as claimed in Claim 1, substantially as herein described with reference to any of Examples 1 to 3.

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